

FORM PTO-1390

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

ATTORNEY DOCKET NUMBER

IN-5513

U.S. APPLICATION NO. IF KNOWN (SEE 37 CFR 15)

09/914937

INTERNATIONAL APPLICATION NO.

INTERNATIONAL FILING DATE

PRIORITY DATE CLAIMED

PCT/EP00/01932

6 March 2000 (06.03.00)

06. March 1999 (06.03.99)

TITLE OF INVENTION: SOL-GEL COATING FOR SINGLE-LAYER OR MULTI-LAYER VARNISHES

APPLICATION(S) FOR DO/EO/US: Peter BETZ, Wilfried STÜBBE, Horst HINTZE-BRÜNING, Heinz-Peter RINK

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
- ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371 (b) and PCT Articles 22 and 39(1).
- ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date
- ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ have been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
- ☒ A translation of the International Application into English (35 U.S.C. 371(C)(2)).
- ☒ Amendment to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made
- ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
- ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
- ☐ A translation of the annex to the International Preliminary Examination Report under PCT Article 36

Items 11. to 16. below concern other document(s) or information included:


11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
13. ☒ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A Change of power of attorney and/or address letter.
16. ☒ Other items or information:

A copy of the cover sheet from the PCT Published Application
A copy of the Priority Document

I hereby certify that the attached correspondence is being deposited with the United States Postal Service in an envelope as "Express Mail Post Office to Addressee" Mailing Label No. **ET115236178 US** addressed to the Commissioner for Patents, Washington, D.C. 20231 on September 5, 2001.

Marjorie Ellis

Marjorie Ellis

U.S. APPLICATION NO. (If known use 37 CFR 1.55) 09/914937		INTERNATIONAL APPLICATION NO. PCT/EP00/01932		ATTORNEY'S DOCKET NUMBER IN-5513	
17. <input checked="" type="checkbox"/> The following fees are submitted				CALCULATIONS PTO USE ONLY	
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) Nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO.....				\$970.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO.....				\$860.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.44(a)(2)) paid to USPTO.....				\$690.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4).....				\$670.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)				\$ 96.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$860.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$130.00	
Claims	Number Filed	Number Extra	Rate		
Total Claims	33 - 20 =	13	X \$18.00	\$234.00	
Independent claims	02 - 03 =	0	X \$80.00	\$	
Multiple dependent claims(s) (if applicable)			+ \$270.00	\$	
TOTAL OF ABOVE CALCULATION =				\$1,224.00	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$1,224.00	
Processing fee of \$130.00 for furnishing the English translation later the <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$1,224.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
TOTAL FEES ENCLOSED =				\$1,224.00	
				Amount to be: refunded	\$
				Charged	\$1,224.00
a. <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed. b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>23-3425</u> in the amount of <u>\$1,224.00</u> to cover the above fees A triplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>23-3425</u> . A triplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO: BASF CORPORATION Patent Department 26701 Telegraph Road Southfield, Michigan 48034-2442 (248) 948-2355			 _____ SIGNATURE Michel F. Morgan Name 42,906 REGISTRATION NUMBER Customer No. 26922		

PATENT
(Practitioner's Docket No. IN- 5513)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Peter BETZ
Wilfried STÜBBE
Horst HINTZE-BRÜNING
Heinz-Peter RINK

Serial No.: This application is a National
Phase of Patent Application PCT/EP00/01932
filed 06. March 2000.

Filed: August 28, 2001

For: SOL-GEL COATING FOR
SINGLE-LAYER OR MULTI-LAYER
VARNISHES

Group Art Unit: Not Assigned

Examiner: Not Assigned

I hereby certify that the attached correspondence is
being deposited with the United States Postal Service in an
envelope as "Express Mail Post Office to Addressee" Mailing
Label No. **ET115236178US** addressed to the BOX PATENT
APPLICATION, Commissioner for Patents, Washington,
D.C. 20231 on 09/05/2001.


Marjorie Ellis

PRELIMINARY AMENDMENT UNDER 37 CFR § 1.115

BOX PATENT APPLICATION
Commissioner for Patents
Washington, D.C. 20231

Sir:

This preliminary amendment is submitted with the application for entry into the U.S.
National Phase under Chapter II. This application is based on PCT/EP00/01932 filed on 6
March 2000.

In connection with the filing of this National Phase application, please make the
following preliminary amendments.

IN THE CLAIMS:

Please substitute claims 1-18 as follows. As required by 37 C.F.R. §1.121, marked
copies of the claims showing amendments for claims 1-18 are listed below.

1. (Amended) A sol-gel coating material comprising
- (A) an acrylate copolymer solution comprising a reaction product of:
- a1) at least one (meth)acrylic ester that is substantially free of acid groups,
 - a2) at least one ethylenically unsaturated monomer that carries at least one hydroxyl group per molecule and is substantially free of acid groups, and
 - a3) at least one ethylenically unsaturated monomer that carries per molecule at least one acid group that can be converted into a corresponding acid anion group;
- (B) a stock varnish comprising a hydrolysis and condensation product of at least one hydrolyzable silane of the general formula I



in which the variable R has the following definition:

R = hydrolyzable groups, hydroxy groups, and nonhydrolyzable groups, with the proviso that at least one hydrolyzable group is present; and

- (C) an additive solution comprising
- c1) at least one ethylenically unsaturated compound containing at least one epoxide group,
 - c2) at least one silane having at least one nonhydrolyzable group R that contains at least one epoxide group, and
 - c3) at least one adduct of the at least one silane having at least one nonhydrolyzable group R that contains at least one amino group and at least one cyclic ethylenically unsaturated dicarboxylic anhydride.
2. (Amended) The sol-gel coating material of claim 1, wherein the sol-gel coating material comprises, based on its overall amount, from 5 to 20% by weight of the acrylate copolymer solution, from 40 to 85% by weight of the stock varnish, and from 0.5 to 3% by weight of the additive solution.
3. (Amended) The sol-gel coating material of claim 1, wherein the sol-gel coating material has a solids contents of the acrylate copolymer solution (A), stock varnish (B), and additive solution (C) in a weight ratio of (A) : (B) : (C) of (1 to 10) : (30 to 60) : (1).

4. (Amended) The sol-gel coating material of claim 1, wherein the stock varnish comprises at least one hydrolyzable metal compound of the general formula II



wherein:

M = aluminum, titanium, or zirconium,

R = hydrolyzable groups, hydroxy groups, and non- hydrolyzable groups, with the proviso that at least one hydrolyzable group is present, and

n = 3 or 4.

5. (Amended) The sol-gel coating material of claim 1, wherein the nonhydrolyzable groups R are at least one of alkyl groups; alkenyl groups; alkynyl groups; and aryl groups; and the hydrolyzable groups R are at least one of hydrogen atoms; alkoxy groups; alkoxy-substituted alkoxy groups having from 3 to 20 carbon atoms; acyloxy groups; and alkylcarbonyl groups.
6. (Amended) The sol-gel, coating material of claim 5, wherein the hydrolyzable groups R are at least one of methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, sec-butoxy, beta-methoxyethoxy, acetox, propionyloxy, and acetyl groups; and the nonhydrolyzable groups R are at least one of methyl, ethyl, propyl, butyl vinyl, 1-propenyl, 2-propenyl, butenyl, acetylenyl, propargyl, phenyl, and naphthyl groups.
7. (Amended) The sol-gel coating material of claim 1, wherein the nonhydrolyzable group R contains at least one functional group.
8. (Amended) The sol-gel coating material of claim 1, wherein the sol-gel coating material is a sol-gel clearcoat material.
9. (Amended) A method comprising applying the sol-gel coating material of claim 1 to a substrate to produce a scratch-resistant sol-gel coating.

10. (Amended) The method of claim 9, wherein the coating is fully cured.
11. (Amended) The method of claim 9, wherein the coating is one of an automotive OEM coating, an automotive refinish coating, an industrial coating, a container coating, a plastic coating, and a furniture coating.
12. (Amended) A process for producing scratch-resistant sol-gel coatings comprising applying and curing the sol-gel coating material of claim 1 on one of a primed substrate, an unprimed substrate, an unprimed substrate comprising a single- or multi-coat paint system, and a primed substrate comprising a single- or multi-coat paint system.
13. (Amended) A process for producing scratch-resistant sol-gel coatings comprising applying and curing a sol-gel coating material on one of an unprimed substrate and a primed substrate, wherein prior to the applying of the sol-gel coating material, at least one of:
- (i1) a single-coat paint system that is at least one of a one-component clearcoat material, a two-component clearcoat material, a multicomponent clearcoat material, a two-component powder clearcoat material, a multicomponent clearcoat material, a two component UV-curable clearcoat material, and a multicomponent UV-curable clearcoat material;
 - (i2) at least one of a multicoat color paint system and a multicoat effect paint system comprising a topmost coat comprising at least one of a one-component clearcoat material, a two-component clearcoat material, a multicomponent clearcoat material, a two component powder clearcoat material, a multicomponent powder clearcoat material, a two component UV-curable clearcoat material, and a multicomponent UV-curable clearcoat material; and
 - (i3) at least one of a single-coat color paint system comprising a two-component solid-color topcoat material and a single-coat effect paint system comprising a two-component solid-color topcoat material;
- is applied and at least partially cured.

14. (Amended) The process of claim 13, wherein the sol-gel coating material comprises

(A) an acrylate copolymer solution comprising a reaction product of:

- a1) at least one (meth)acrylic ester that is substantially free of acid groups,
- a2) at least one ethylenically unsaturated monomer that carries at least one hydroxyl group per molecule and is substantially free of acid groups, and
- a3) at least one ethylenically unsaturated monomer that carries per molecule at least one acid group that can be converted into the corresponding acid anion group;

(B) a stock varnish comprising a hydrolysis and condensation product of at least one hydrolyzable silane of the general formula I



in which the variable R has the following definition:

R = hydrolyzable groups, hydroxy groups, and nonhydrolyzable groups, with the proviso that at least one hydrolyzable group is present; and

(C) an additive solution comprising

- c1) at least one ethylenically unsaturated compound containing at least one epoxide group,
- c2) at least one silane having at least one nonhydrolyzable group R that contains at least one epoxide group, and
- c3) at least one adduct of the at least one silane having at least one nonhydrolyzable group R that contains at least one amino group and at least one cyclic ethylenically unsaturated dicarboxylic anhydride.

15. (Amended) The process of claim 12, wherein the applied sol-gel coating material is cured by exposure to middle-range IR radiation.

16. (Amended) The process of claim 12, wherein the paint system is at least one of an automotive OEM paint system, an automotive refinish paint system, an industrial coating paint system, a container coating paint system, and a furniture coating paint system.

17. (Amended) A sol-gel coating comprising the sol-gel coating material of claim 1.
18. (Amended) A substrate comprising at least one sol-gel coating of claim 17.

Please insert the following new claims:

19. (New) The sol-gel coating material of claim 7, wherein the at least one functional group is at least one of an epoxide group, an amino group, an olefinically unsaturated group, a mercapto group, an isocyanate group, and a reaction product of any of the preceding with further reactive compounds.

20. (New) The sol-gel coating material of claim 1, wherein at least two of:

- a. the sol-gel coating material comprises, based on its overall amount, from 5 to 20% by weight of the acrylate copolymer solution, from 40 to 85% by weight of the stock varnish, and from 0.5 to 3% by weight of the additive solution;
- b. the sol-gel coating material has a solids contents of the acrylate copolymer solution (A), stock varnish (B), and additive solution (C) in a weight ratio of (A) : (B) : (C) of (1 to 10) : (30 to 60) : (1);
- c. the stock varnish comprises at least one hydrolyzable metal compound of the general formula II



wherein:

M = aluminum, titanium, or zirconium,

R = hydrolyzable groups, hydroxy groups, and non- hydrolyzable groups, with the proviso that at least one hydrolyzable group is present, and

n = 3 or 4

- d. the nonhydrolyzable groups R are at least one of alkyl groups; alkenyl groups; alkynyl groups; and aryl groups; and the hydrolyzable groups R are at least one of hydrogen atoms; alkoxy groups; alkoxy-substituted alkoxy groups having from 3 to 20 carbon atoms; acyloxy groups; and alkylcarbonyl groups;
- e. the nonhydrolyzable groups R contain at least one functional group; and
- f. the sol-gel coating material is a sol-gel clearcoat material.

21. (New) The sol-gel coating material of claim 20, wherein at least one of:

- a. the hydrolyzable groups R are at least one of methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, sec-butoxy, beta-methoxyethoxy, acetoxy, propionyloxy, and acetyl groups; and the nonhydrolyzable groups R are at least one of

methyl, ethyl, propyl, butyl vinyl, 1-propenyl, 2-propenyl, butenyl, acetylenyl, propargyl, phenyl, and naphthyl groups; and

- b. the at least one functional group is at least one of an epoxide group, an amino group, an olefinically unsaturated group, a mercapto group, an isocyanate group, and a reaction product thereof with further reactive compounds.
22. (New) A sol-gel coating comprising the sol-gel coating material of claim 20.
23. (New) A substrate comprising at least one sol-gel coating of claim 22.
24. (New) The process of claim 14, wherein at least one of:
- a. the sol-gel coating material comprises, based on its overall amount, from 5 to 20% by weight of the acrylate copolymer solution, from 40 to 85% by weight of the stock varnish, and from 0.5 to 3% by weight of the additive solution;
 - b. the sol-gel coating material has a solids contents of the acrylate copolymer solution (A), stock varnish (B), and additive solution (C) in a weight ratio of (A) : (B) : (C) of (1 to 10) : (30 to 60) : (1);
 - c. the stock varnish comprises at least one hydrolyzable metal compound of the general formula II
$$\text{MR}_n \quad (\text{II}),$$
wherein:
$$\text{M} = \text{aluminum, titanium, or zirconium,}$$
$$\text{R} = \text{hydrolyzable groups, hydroxy groups, and non- hydrolyzable groups,}$$
with the proviso that at least one hydrolyzable group is present, and
$$n = 3 \text{ or } 4$$
 - d. the nonhydrolyzable groups R are at least one of alkyl groups; alkenyl groups; alkynyl groups; and aryl groups; and the hydrolyzable groups R are at least one of hydrogen atoms; alkoxy groups; alkoxy-substituted alkoxy groups having from 3 to 20 carbon atoms; acyloxy groups; and alkylcarbonyl groups;
 - e. the nonhydrolyzable groups R contain at least one functional group; and
 - f. the sol-gel coating material is a sol-gel clearcoat material.

25. (New) The process of claim 24, wherein at least one of:
- a. the hydrolyzable groups R are at least one of methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, sec-butoxy, beta-methoxyethoxy, acetoxy, propionyloxy, and acetyl groups; and the nonhydrolyzable groups R are at least one of methyl, ethyl, propyl, butyl vinyl, 1-propenyl, 2-propenyl, butenyl, acetylenyl, propargyl, phenyl, and naphthyl groups; and
 - b. the at least one functional group is at least one of an epoxide group, an amino group, an olefinically unsaturated group, a mercapto group, an isocyanate group, and a reaction product thereof with further reactive compounds.
26. (New) A sol-gel coating produced by the process of claim 24.
27. (New) A substrate comprising at least one sol-gel coating of claim 26.
28. (New) A sol-gel coating produced by the process of claim 12.
29. (New) A substrate comprising at least one sol-gel coating of claim 28.
30. (New) A sol-gel coating produced by the process of claim 13.
31. (New) A substrate comprising at least one sol-gel coating of claim 30.
32. (New) A sol-gel coating produced by the process of claim 14.
33. (New) A substrate comprising at least one sol-gel coating of claim 32.

Version with Markings to Show Changes Made

As is permitted by 37 C.F.R. §1.121(c)(1)(ii), amendments to the claims are shown by an equivalent marking system. Insertions are still shown by underline, and deletions are shown by strikethrough.

1. (Amended) A sol-gel coating material comprising
 - (A) an acrylate copolymer solution comprising ~~at least one acrylate copolymer (A1)~~ preparable by copolymerizing at least the following monomers a reaction product of:
 - a1) at least one (meth)acrylic ester ~~which~~that is substantially free of acid groups,
 - a2) at least one ethylenically unsaturated monomer ~~which~~that carries at least one hydroxyl group per molecule and is substantially free of acid groups, and
 - a3) at least one ethylenically unsaturated monomer ~~which~~that carries per molecule at least one acid group ~~which~~that can be converted into ~~the a~~ corresponding acid anion group;
 - (B) a stock varnish ~~preparable by hydrolyzing and condensing~~comprising a hydrolysis and condensation product of at least one hydrolyzable silane ~~(E1)~~ of the general formula I
$$\text{SiR}_4 \quad (\text{I}),$$
in which the variable R has the following definition:

R = hydrolyzable groups, hydroxy groups, and nonhydrolyzable groups, with the proviso that at least one, ~~preferably at least two,~~ hydrolyzable group(s) is ~~or are~~ present; and
 - (C) an additive solution comprising
 - c1) at least one ethylenically unsaturated compound containing at least one epoxide group,
 - c2) at least one silane ~~(B1)~~ having at least one nonhydrolyzable group R ~~which~~that contains at least one epoxide group, and
 - c3) at least one adduct of the at least one silane ~~(B1)~~ having at least one nonhydrolyzable group R ~~which~~that contains at least one amino group

and at least one cyclic ethylenically unsaturated dicarboxylic anhydride.

2. (Amended) The sol-gel coating material of claim 1, ~~characterized in that it~~wherein the sol-gel coating material comprises, based ~~in each case on~~ its overall amount, from 5 to 20, ~~preferably from 10 to 15 and in particular from 11 to 14%~~ by weight of the acrylate copolymer solution (A), from 40 to 85, ~~preferably from 45 to 80, and in particular from 50 to 75%~~ by weight of the stock varnish (B), and from 0.5 to 3, ~~preferably from 1 to 2, and in particular from 1.2 to 1.7%~~ by weight of the additive solution (C).
3. (Amended) The sol-gel coating material of claim 1 ~~or 2, characterized in that~~wherein the sol-gel coating material has a solids contents of the constituents acrylate copolymer solution (A), stock varnish (B), and additive solution (C) are in a weight ratio of (A) : (B) : (C) of
- (1 to 10) : (30 to 60) : (1)
- ~~preferably 2 to 8 : 35 to 55 : 1, and~~
- ~~in particular 2.5 to 6 : 40 to 50 : 1.~~
4. (Amended) The sol-gel coating material of ~~one of claims 1 to 3, characterized in that~~wherein the stock varnish (B) ~~comprises at least one hydrolyzable metal compound of the general formula II~~
- $$\text{MR}_n \quad (\text{II}),$$
- ~~in which the variables and the index have the following definition~~wherein:
- M = aluminum, titanium, or zirconium,
- R = hydrolyzable groups, hydroxy groups, and non- hydrolyzable groups, with the proviso that at least one, ~~preferably at least two,~~ hydrolyzable group(s) is ~~or are~~ present, and
- n = 3 or 4.
5. (Amended) The sol-gel coating material of ~~one of claims 1 to 4, characterized in that~~wherein

——the nonhydrolyzable groups R are at least one of alkyl groups, especially having from 1 to 4 carbon atoms; alkenyl groups, especially having from 2 to 4 carbon atoms; —alkynyl groups especially having from 2 to 4 carbon atoms; and/or aryl groups, especially having from 6 to 10 carbon atoms; and

——the hydrolyzable groups R are at least one of hydrogen atoms; alkoxy groups, especially having from 1 to 20 carbon atoms; alkoxy-substituted alkoxy groups having from 3 to 20 carbon atoms; acyloxy groups, especially having from 1 to 4 carbon atoms; and alkylcarbonyl groups, especially having from 2 to 6 carbon atoms.

6. (Amended) The sol-gel, coating material of claim 5, ~~characterized in that wherein~~
——the hydrolyzable groups R are at least one of methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, sec-butoxy, beta-methoxyethoxy, acetoxy, propionyloxy, and/or acetyl groups; and the
——the nonhydrolyzable groups R are at least one of methyl, ethyl, propyl, butyl vinyl, 1-propenyl, 2-propenyl, butenyl, acetylenyl, propargyl, phenyl, and/or and naphthyl groups.
7. (Amended) The sol-gel coating material of ~~one of~~ claims 1 to 6, ~~characterized in that~~wherein the nonhydrolyzable groups R contains at least one functional group, in particular at least one epoxide group, amino group, olefinically unsaturated group, mercapto group, and/or isocyanate group and/or reaction products thereof with further reactive compounds.
8. (Amended) The sol-gel coating material of ~~one of~~ claims 1 to 7, ~~characterized in that~~wherein ~~it~~the sol-gel coating material is a sol-gel clearcoat material.
9. (Amended) ~~The use of~~A method comprising applying the sol-gel coating material ~~in accordance with one of claims 1 to 8 to a substrate to produce a scratch-resistant sol-gel coatings, especially for single coat or multicoat paint systems.~~
10. (Amended) ~~The use of the sol-gel coating material~~method of claim 9, ~~characterized in that~~wherein the paint systems in question ~~coating are~~is fully cured single coat or multicoat paint systems.

11. (Amended) ~~The use of the sol-gel coating material method~~ of claim 9 ~~or 10~~, characterized in that ~~the paint systems are~~ wherein the coating is one of an automotive OEM paint systemscoating, an automotive refinish paint systemscoating, an industrial paint systemscoating, including a container coatings, a plastic coatings on plasties, and a furniture coatings.

12. (Amended) A process for producing scratch-resistant sol-gel coatings bycomprising applying and curing the sol-gel coating materials of claim 1 on one of a primed substrate, or an unprimed substrates, or an unprimed substrate comprising a single- or multi-coat paint system, or and a primed substrates comprising a single- or multi-coat paint system ~~provided with a single coat or multicoat paint system,~~ characterized in that ~~a sol-gel coating material in accordance with one of claims 1 to 8 is used in this process.~~

13. (Amended) A process for producing scratch-resistant sol-gel coatings bycomprising applying and curing a sol-gel coating materials on one of an unprimed substrate or and a primed substrates ~~which have been provided with a single coat or multicoat paint system,~~ characterized in that, wherein prior to the ~~application~~ applying of the sol-gel coating material, at least one of:
 - (i1) ~~a single-coat paint system based on~~ that is at least one of a one-component (1K) clearcoat material, a two-component (2K) clearcoat material, or a multicomponent (3K, 4K) clearcoat material, a two-component powder clearcoat material, a multicomponent clearcoat material, or a two component UV-curable clearcoat material, and a multicomponent UV-curable clearcoat material;
 - (i2) at least one of a multicoat color and/or effect paint system and a multicoat effect paint system with comprising a topmost coat based on comprising at least one of a one-component (1K) clearcoat material, a two-component (2K) clearcoat material, or a multicomponent (3K, 4K) clearcoat material, a two component powder clearcoat material, a multicomponent powder clearcoat material, or a two component UV-curable clearcoat material, and a multicomponent UV-curable clearcoat material; and especially a one-

~~component (1K) clearcoat material, two-component (2K) or multicomponent (3K,4K) clearcoat material, or~~

- (i3) at least one of a single-coat color and/or effect paint system comprising a two-component solid-color topcoat material and a single-coat effect paint system based on comprising a two-component (2K)-solid-color topcoat material;
is applied and ~~partly~~ at least partially cured.

14. (Amended) The process of claim 13, ~~characterized in that~~ wherein ~~the~~ sol-gel coating material ~~comprises in accordance with one of claims 1 to 8 is used in this process:~~

(A) an acrylate copolymer solution comprising a reaction product of:

- a1) at least one (meth)acrylic ester that is substantially free of acid groups,
a2) at least one ethylenically unsaturated monomer that carries at least one hydroxyl group per molecule and is substantially free of acid groups,
and
a3) at least one ethylenically unsaturated monomer that carries per molecule at least one acid group that can be converted into the corresponding acid anion group;

(B) a stock varnish comprising a hydrolysis and condensation product of at least one hydrolyzable silane of the general formula I



in which the variable R has the following definition:

R = hydrolyzable groups, hydroxy groups, and nonhydrolyzable groups,
with the proviso that at least one hydrolyzable group is present; and

(C) an additive solution comprising

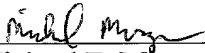
- c1) at least one ethylenically unsaturated compound containing at least one epoxide group,
c2) at least one silane having at least one nonhydrolyzable group R that contains at least one epoxide group, and
c3) at least one adduct of the at least one silane having at least one nonhydrolyzable group R that contains at least one amino group and at least one cyclic ethylenically unsaturated dicarboxylic anhydride.

15. (Amended) The process of ~~one of claims 12 to 14, characterized in that~~wherein the applied sol-gel coating material is cured by exposure to middle-range IR radiation.
16. (Amended) The process of ~~one of claims 12 to 15, characterized in that~~wherein the paint systems ~~are~~is at least one of an automotive OEM paint systems, an automotive refinish paint systems, an industrial coating paint systems, ~~including a~~ container coatings paint system, and a furniture coatings paint system.
17. (Amended) A ~~S~~sol-gel coatings ~~which can be produced from~~comprising the sol-gel coating material ~~in accordance with one of claims 1 to 8 and/or by the process in accordance with one of claims 12 to 16.~~
18. (Amended) A ~~S~~substrates comprising at least one sol-gel coating ~~in accordance with~~of claim 17.

REMARKS

Upon entry of the present amendment claims 1-33 are pending in the application. Claims 1-18 have been amended in accordance with the requirements of U.S. patent practice. New claims 19-33 add no new matter, as these claims contain subject matter deleted from the amended claims. There are 2 independent claims and a total of 33 claims pending in the application. Applicants respectfully request entry of the preliminary amendment.

Respectfully Submitted,



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Sol-gel coating for single-coat or multicoat paint systems

The present invention relates to a novel sol-gel
5 coating material for producing sol-gel coatings on
single-coat or multicoat paint systems. The present
invention particularly relates to a novel process for
producing painted substrates, especially painted
automobile bodies, in which the substrates are first
10 provided with a multicoat paint system to which a sol-
gel coating material is then applied and cured.

Automobile bodies are provided extensively with a
multicoat color and/or effect paint system. Clearcoats
15 are frequently applied as the final coat. Materials
suitable for this purpose are the customary and known
two-component (2K) or multicomponent (3K, 4K) clearcoat
materials.

20 Two-component (2K) or multicomponent (3K, 4K) clearcoat
materials are known to include as their key constituents
binders having functional groups which are able to
react with isocyanate groups and polyisocyanate cross-
linking agents containing free isocyanate groups. The
25 two key constituents are stored separately until their
use. Both aqueous and conventional two component (2K)
or multicomponent (3K, 4K) clearcoat materials are
known. An example of an aqueous system is disclosed by

the German patent DE-A-44 21 823. These clearcoat materials give weathering-stable coatings which, however, are often not sufficiently scratch-resistant under severe stress. Scratches are particularly
5 visually disruptive even when the clearcoat surface is merely deformed, without any material being removed.

The automobile bodies, especially those for commercial vehicles, may, however, also have single-coat color
10 and/or effect paint systems, which are referred to as solid-color topcoats. Both one-component (1K) and two-component (2K) solid-color topcoat materials are employed. As is known, the one-component (1K) solid-color topcoat materials comprise self-crosslinking or
15 externally crosslinking binders and, for example, amino resin or blocked polyisocyanate crosslinking agents. The two-component (2K) solid-color topcoat materials contain binders with functional groups that are able to react with isocyanate groups, and polyisocyanate cross-
20 linking agents containing free isocyanate groups. Coating materials of this kind are also used as automotive refinish materials. As with the two-component (2K) clearcoat materials, their two essential components are stored separately from one another
25 before use. Solid-color topcoats have a scratch resistance which in some cases fails to satisfy the particularly severe stress to which commercial vehicles are often exposed.

More recently, materials known as sol-gel clearcoats and based on siloxane-containing coating formulations have been developed which are obtained by hydrolysis and condensation of silane compounds. These coating materials, which are used as coating compositions on plastics, are described, for example, in the German patents DE-A-43 03 570, 34 07 087, 40 11 045, 40 25 215, 38 28 098, 40 20 316, and 41 22 743.

10 Sol-gel clearcoats impart very good scratch resistance to substrates made of plastic, such as spectacle lenses or motorcycle helmet visors, for example. This scratch resistance is not achieved by the known OEM (original equipment manufacturing) clearcoat materials normally used for the original finishing of vehicles. The automobile industry is now demanding that this improved scratch resistance be transferred to the clearcoats and solid-color topcoats used in the finishing of automobiles, as well.

20

Replacing the OEM clearcoat materials commonly used in automotive finishing by sol-gel clearcoat materials, however, is not immediately possible, since the clearcoats are too brittle for this purpose, for example, or because the optical properties (appearance) achieved during the attempt to adapt them to the OEM requirements are in many cases poor. In particular, the sol-gel clearcoat materials are too expensive. The economically more favorable use of the sol-gel

clearcoat materials as an additional coat over the clearcoats or solid-color topcoats used to date gives rise to adhesion problems between these paint systems and the sol-gel coat, these problems arising in particular after stone chipping and on exposure to condensation.

It is an object of the present invention to provide a novel sol-gel coating material which permits combination of the advantageous properties of the sol-gel coatings and the advantageous properties of the known single-coat or multicoat paint systems, especially the single-coat or multicoat color and/or effect paint systems for automotive OEM finishing, without any adhesion problems.

The invention accordingly provides the novel sol-gel coating material comprising

(A) an acrylate copolymer solution comprising at least one acrylate copolymer (A1) preparable by copolymerizing at least the following monomers:

a1) at least one (meth)acrylic ester which is substantially free of acid groups,

a2) at least one ethylenically unsaturated monomer which carries at least one hydroxyl

group per molecule and is substantially free of acid groups, and

5 a3) at least one ethylenically unsaturated monomer which carries per molecule at least one acid group which can be converted into the corresponding acid anion group;

10 (B) a stock varnish preparable by hydrolyzing and condensing at least one hydrolyzable silane (B1) of the general formula I



15 in which the variable R has the following definition:

R = hydrolyzable groups, hydroxy groups and non-hydrolyzable groups, with the proviso that at
20 least one, preferably at least two, hydrolyzable group(s) is or are present;

and

25 (C) an additive solution comprising

c1) at least one ethylenically unsaturated compound containing at least one epoxide group,

c2) at least one silane (B1) having at least one nonhydrolyzable group R which contains at least one epoxide group, and

- 5 c3) at least one adduct of at least one silane (B1) having at least one nonhydrolyzable group R which contains at least one amino group and at least one cyclic ethylenically unsaturated dicarboxylic anhydride.

10

In the text below, the novel sol-gel coating material is referred to as the "coating material of the invention".

- 15 The invention further provides the novel process for producing sol-gel coatings by applying and curing sol-gel coating materials to primed or unprimed substrates or unprimed or primed substrates which have been provided with a single-coat or multicoat paint system,
20 in which process the coating material of the invention is used and/or in which, prior to the application of a sol-gel coating material,

- (i1) a single-coat paint system based on a one-
25 component (1K) clearcoat material, two-component (2K) or multicomponent (3K, 4K) clearcoat material, powder clearcoat material or UV-curable clearcoat material,

(i2) a multicoat color and/or effect paint system with
a topmost coat based on a one-component (1K)
clearcoat material, two-component (2K) or multi-
component (3K, 4K) clearcoat material, powder
5 clearcoat material or UV-curable clearcoat
material, or

(i3) a single-coat color and/or effect paint system
based on a solid-color topcoat material

10

is applied and partly cured.

In the following, the novel processes for producing
sol-gel coatings are referred to collectively, for the
15 sake of brevity, as the "process of the invention".

The invention additionally provides novel sol-gel
coatings which can be produced from the coating
materials of the invention and which are referred to
20 below as "sol-gel coatings of the invention".

The invention provides not least novel substrates which
have at least one sol-gel coating of the invention and
are referred to below as "substrates of the invention".

25

In the light of the prior art it was surprising and
unforeseeable for the skilled worker that the object on
which the invention is based could be achieved by means
of the coating material of the invention and process of

the invention. A particular surprise was that the coating material of the invention adheres without problems to the paint systems without instances of delamination or cracking on stone chipping or following
5 exposure to condensation, i.e., ten-day exposure of the coats in an atmosphere of 40°C and 100% relative atmospheric humidity. Additionally, the optical properties of the paint systems provided with the sol-gel coatings of the invention meet all requirements.

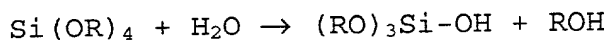
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The coating material of the invention comprises a siloxane-containing coating formulation which can be prepared by reacting hydrolyzable silicon compounds with water or water donors and which comprises organic
15 constituents in order to improve certain properties. A general description of such systems is given, for example, in the article by Bruce M. Novak, "Hybrid Nanocomposite Materials - Between Inorganic Glasses and Organic Polymers", in Advanced Materials, 1993, 5, No. 6, pp. 422-433, or in the presentation by R. Kasemann, H. Schmidt, 15th International Conference, International Centre for Coatings Technology, Paper 7, "Coatings for mechanical and chemical protection based
20 on organic-inorganic sol-gel nanocomposites", 1993.

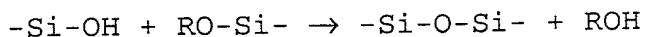
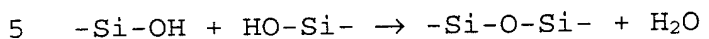
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The base reactions take place in a sol-gel process in which tetraorthosilicates are hydrolyzed and condensed in the presence or absence of a cosolvent:

Hydrolysis:



Condensation:



where R can be an alkyl group, such as methyl or ethyl. Frequently, tetramethyl orthosilicate (TMOS) or
10 tetraethyl orthosilicate (TEOS) are used. To catalyze the reactions, acids, bases or fluoride ions are used.

The coating material of the invention thus comprises siloxane-containing structures modified with organic
15 constituents (Ormocer® = organically modified ceramic).

By means of controlled hydrolysis and condensation of silicic esters and of metal alkoxides, the sol-gel coating of the invention is prepared. It acquires
20 specific properties through the incorporation of organically modified silicic acid derivatives into the silicatic network. They permit the construction of an organic polymer network in addition to the inorganic framework, if organic radicals, preferably those
25 containing olefinically unsaturated groups and/or epoxide groups, are used.

Modification is inventively effected as a result of the presence of a ready-made organic polymer during the

hydrolysis and condensation of the starting materials or in the sol.

The coating material of the invention consists of the
5 three essential components (A), (B) and (C).

Component (A) comprises an acrylate copolymer solution which is preferably free of aromatic solvents.

10 In the context of the present invention, the term "free of aromatic solvents" or "aromatics-free", here and below, means that the amount of aromatic solvents or aromatic compounds in a solution is < 1% by weight, preferably < 0.5% by weight, and with particular
15 preference < 0.2% by weight, and in particular lies below the gas-chromatographic detection limit.

The acrylate copolymer solution (A) for inventive use comprises at least one acrylate copolymer (A1) prepared
20 by copolymerizing the following monomers (a1), (a2) and (a3) and also, if desired, further monomers (a4), (a5) and/or (a6), the nature and amount of (a1), (a2) and (a3) and also, if used, (a4), (a5) and (a6) being selected such that the acrylate copolymer (A1) has the
25 desired OH number and acid number and the desired molecular weight. Preferably, the acrylate copolymers (A1) have a hydroxyl number of from 40 to 240, with particular preference from 60 to 210, and in particular from 100 to 200, an acid number of from 5 to 100, with

particular preference from 10 to 60, and in particular from 20 to 40, glass transition temperatures of from -35° to +85°C, and number-average molecular weights M_n of from 1 500 to 300 000.

5

The polyacrylate resins used inventively may be prepared using as monomer (a1) any (meth)acrylic acid alkyl or cycloalkyl ester which is copolymerizable with (a2), (a3), (a4), (a5) and (a6) and has up to 20 carbon atoms in the alkyl radical, especially methyl, ethyl, propyl, n-butyl, sec-butyl, tert-butyl, hexyl, ethylhexyl, stearyl and lauryl acrylate or methacrylate; cycloaliphatic (meth)acrylates, especially cyclohexyl, isobornyl, dicyclopentadienyl, octahydro-4,7-methano-1H-indenemethanol or tert-butylcyclohexyl (meth)acrylate; (meth)acrylic oxaalkyl or oxacycloalkyl esters such as ethyltriglycol (meth)acrylate and methoxyoligoglycol (meth)acrylate having a molecular weight Mn of preferably 550; or other ethoxylated and/or propoxylated, hydroxyl-free (meth)acrylic acid derivatives. These monomers may include, in minor amounts, more highly functional (meth)acrylic alkyl or cycloalkyl esters such as ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, butylene glycol, 1,5-pentanediol, 1,6-hexanediol, octahydro-4,7-methano-1H-indenedimethanol or 1,2-, 1,3- or 1,4-cyclohexanediol di(meth)acrylate; trimethylolpropane di- or tri(meth)acrylate; or pentaerythritol di-, tri- or tetra(meth)acrylate. In the context of the present invention,

minor amounts of higher-functional monomers are those amounts that do not lead to crosslinking or gelling of the polyacrylate resins.

- 5 As monomers (a2) it is possible to use any ethylenically unsaturated monomers which are copolymerizable with (a1), (a2), (a3), (a4), (a5) and (a6) and different from (a5), carry at least one hydroxyl group per molecule and are essentially free from acid groups, such as
- 10 hydroxyalkyl esters of acrylic acid, methacrylic acid or another alpha,beta-ethylenically unsaturated carboxylic acid which are derived from an alkylene glycol which is esterified with the acid or are obtainable by reacting the acid with an alkylene oxide;
- 15 especially hydroxyalkyl esters of acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid or itaconic acid, in which the hydroxyalkyl group contains up to 20 carbon atoms, such as 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl,
- 20 3-hydroxybutyl, 4-hydroxybutyl acrylate, methacrylate, ethacrylate, crotonate, maleate, fumarate or itaconate; 1,4-bis(hydroxymethyl)cyclohexane, octahydro-4,7-methano-1H-indenedimethanol or methylpropanediol monoacrylate, monomethacrylate, monoethacrylate, monocrotonate, mono-
- 25 maleate, monofumarate or monoitaconate; or reaction products of cyclic esters, such as epsilon-caprolactone, for example, and these hydroxyalkyl esters; or olefinically unsaturated alcohols such as allyl alcohol or polyols such as trimethylolpropane monoallyl or

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diallyl ether or pentaerythritol monoallyl, diallyl or triallyl ether. As far as these higher-functional monomers (a2) are concerned, the comments made for the higher-functional monomers (a1) apply analogously. The proportion of trimethylolpropane monoallyl ether is usually from 2 to 10% by weight, based on the overall weight of the monomers (a1) to (a6) used to prepare the polyacrylate resin. In addition, however, it is also possible to add from 2 to 10% by weight, based on the overall weight of the monomers used to prepare the polyacrylate resin, of trimethylolpropane monoallyl ether to the finished polyacrylate resin. The olefinically unsaturated polyols, such as trimethylolpropane monoallyl ether in particular, may be used as sole hydroxyl-containing monomers, but in particular may be used proportionately in combination with other of the abovementioned hydroxyl-containing monomers.

As the monomer (a3) it is possible to use any ethylenically unsaturated monomer, or mixture of such monomers, which carries at least one acid group, preferably one carboxyl group, per molecule and is copolymerizable with (a1), (a2), (a4), (a5) and (a6). As component (a3) it is particularly preferred to use acrylic acid and/or methacrylic acid. However, other ethylenically unsaturated carboxylic acids having up to 6 carbon atoms in the molecule may also be used. Examples of such acids are ethacrylic acid, crotonic acid, maleic acid, fumaric acid, and itaconic acid. It

is further possible to use ethylenically unsaturated sulfonic or phosphonic acids, and/or their partial esters, as component (a3). Further suitable components (a3) include mono(meth)acryloyloxyethyl maleate, 5 succinate and phthalate.

As monomers (a4) it is possible to use one or more vinyl esters of alpha-branched monocarboxylic acids having 5 to 18 carbon atoms in the molecule. The 10 branched monocarboxylic acids may be obtained by reacting formic acid or carbon monoxide and water with olefins in the presence of a liquid, strongly acidic catalyst; the olefins may be cracking products of paraffinic hydrocarbons, such as mineral oil fractions, 15 and may comprise branched and straight-chain acyclic and/or cycloaliphatic olefins. The reaction of such olefins with formic acid or with carbon monoxide and water produces a mixture of carboxylic acids in which the carboxyl groups are located predominantly on a 20 quaternary carbon atom. Other olefinic starting materials are, for example, propylene trimer, propylene tetramer and diisobutylene. Alternatively, the vinyl esters may be prepared in a conventional manner from the acids; for example, by reacting the acid with 25 acetylene. Particular preference, owing to their ready availability, is given to the use of vinyl esters of saturated aliphatic monocarboxylic acids having 9 to 11 carbon atoms which are branched on the alpha carbon atom.

As the monomer (a5), use is made of the reaction product of acrylic acid and/or methacrylic acid with the glycidyl ester of an alpha-branched monocarboxylic acid having 5 to 18 carbon atoms per molecule. Glycidyl esters of highly branched monocarboxylic acids are available under the trade name "Cardura". The reaction of the acrylic or methacrylic acid with the glycidyl ester of a carboxylic acid having a tertiary alpha carbon atom can take place before, during or after the polymerization reaction. As the component (a5) it is preferred to use the reaction product of acrylic acid and/or methacrylic acid with the glycidyl ester of Versatic acid. This glycidyl ester is commercially available under the name "Cardura E10".

As monomers (a6) it is possible to use all ethylenically unsaturated monomers, or mixtures of such monomers, which are copolymerizable with (a1), (a2), (a3), (a4) and (a5), are different from (a1), (a2), (a3) and (a4), and are substantially free from acid groups. Suitable components (a6) include the following:

- olefins such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, cyclohexene, cyclopentene, norbornene, butadiene, isoprene, cyclopentadiene and/or dicyclopentadiene;

- (meth)acrylamides such as (meth)acrylamide, N-methyl-, N,N-dimethyl-, N-ethyl-, N,N-diethyl-,

N-propyl-, N,N-dipropyl-, N-butyl-, N,N-dibutyl-,
N-cyclohexyl- and/or N,N-cyclohexyl-methyl-(meth)-
acrylamide;

- 5 - monomers containing epoxide groups, such as the
glycidyl ester of acrylic acid, methacrylic acid,
ethacrylic acid, crotonic acid, maleic acid,
fumaric acid and/or itaconic acid;
- 10 - vinylaromatic hydrocarbons, such as styrene,
alpha-alkylstyrenes, especially alpha-methyl-
styrene, and/or vinyltoluene;
- nitriles such as acrylonitrile and/or methacrylo-
15 nitrile;
- vinyl compounds such as vinyl chloride, vinyl
fluoride, vinylidene dichloride, vinylidene
difluoride; N-vinylpyrrolidone; vinyl ethers such
20 as ethyl vinyl ether, n-propyl vinyl ether,
isopropyl vinyl ether, n-butyl vinyl ether,
isobutyl vinyl ether and/or vinyl cyclohexyl
ether; vinyl esters such as vinyl acetate, vinyl
propionate, vinyl butyrate, vinyl pivalate and/or
25 the vinyl ester of 2-methyl-2-ethylheptanoic acid;
and/or
- polysiloxane macromonomers having a number-average
molecular weight M_n of from 1 000 to 40 000,

preferably from 2 000 to 20 000, with particular preference from 2 500 to 10 000 and in particular from 3 000 to 7 000 and having on average from 0.5 to 2.5, preferably from 0.5 to 1.5, ethylenically unsaturated double bonds per molecule, as described in DE-A-38 07 571 on pages 5 to 7, in DE-A-37 06 095 in columns 3 to 7, in EP-B-0 358 153 on pages 3 to 6, in US-A-4,754,014 in columns 5 to 9, in DE-A-44 21 823 or in the international patent application WO 92/22615 on page 12, line 18 to page 18, line 10, or acryloxysilane-containing vinyl monomers, preparable by reacting hydroxy-functional silanes with epichlorohydrin and subsequently reacting the reaction product with methacrylic acid and/or hydroxyalkyl esters of (meth)acrylic acid.

Preference is given to using vinylaromatic hydrocarbons, especially styrene.

20

The nature and amount of the components (a1) to (a6) is selected such that the polyacrylate resin (A1) has the desired OH number, acid number, and glass transition temperature. Acrylate resins used with particular preference are obtained by polymerizing

(a1) from 20 to 60% by weight, preferably from 30 to 50% by weight, of the component (a1),

(a2) from 10 to 50% by weight, preferably from 15 to 40% by weight, of the component (a2),

(a3) from 1 to 15% by weight, preferably from 1 to 8%
5 by weight, of the component (a3),

(a4) from 0 to 25% by weight of the component (a4),

(a5) from 0 to 25% by weight of the component (a5), and
10

(a6) from 5 to 30% by weight, preferably from 10 to 20%
by weight, of the component (a6),

the sum of the weight fractions of the components (a1)
15 to (a6) being 100% in each case.

The inventively employed acrylate copolymers (A1) are prepared in an organic solvent or solvent mixture, which is preferably free from aromatic solvents, and in
20 the presence of at least one polymerization initiator. Polymerization initiators used are the polymerization initiators which are customary for the preparation of acrylate copolymers.

25 Examples of suitable polymerization initiators are initiators which form free radicals, such as, for example, tert-butyl peroxyethylhexanoate, benzoyl peroxide, di-tert-amyl peroxide, azobisisobutyronitrile, and tert-butyl perbenzoate. The initiators are

used preferably in an amount of from 1 to 25% by weight, with particular preference from 2 to 10% by weight, based on the overall weight of the monomers.

- 5 The polymerization is appropriately conducted at a temperature of from 80 to 200°C, preferably from 110 to 180°C.

Preferred solvents used are ethoxyethyl propionate and
10 isopropoxypropanol.

The acrylate copolymer (A1) is preferably prepared by a two-stage process, since in this way the resulting coating materials of the invention have improved
15 processing properties. Preference is therefore given to using acrylate copolymers (A1) which are obtainable by

1. polymerizing a mixture of the monomers (a1) and (a2) and, if desired, (a4), (a5) and/or (a6), or a
20 mixture of portions of the monomers (a1) and (a2) and also, if desired, (a4), (a5) and/or (a6), in an organic solvent, and
2. after at least 60% by weight of the mixture of
25 (a1) and (a2) and, if desired, (a4), (a5) and/or (a6) have been added, adding the monomer (a3) and any remainder of the monomers (a1) and (a2) and, if appropriate, (a4), (a5) and/or (a6), and continuing polymerization.

In addition, however, it is also possible to include the monomers (a4) and/or (a5) in the initial charge, together with at least some of the solvent, and to meter in the remaining monomers. Furthermore, it is
5 also possible for only some of the monomers (a4) and/or (a5) to be included in the initial charge, together with at least some of the solvent, and for the remainder of these monomers to be added as described above. Preferably, for example, at least 20% by weight
10 of the solvent and about 10% by weight of the monomers (a4) and (a5), and, if desired, portions of the monomers (a1) and (a6), are included in the initial charge.

15 Preference is further given to preparing the inventively employed acrylic polymers (A1) by a two-stage process in which the first stage lasts for from 1 to 8 hours, preferably from 1.5 to 4 hours, and the mixture of (a3) and any remainder of the monomers (a1),
20 (a2) and, if appropriate, (a4), (a5) and (a6) is added over the course of from 20 to 120 minutes, preferably over the course of from 30 to 90 minutes. Following the end of the addition of the mixture of (a3) and any remainder of the monomers (a1) and (a2) and, if
25 appropriate, (a4), (a5) and (a6), polymerization is continued until all of the monomers used have undergone substantially complete reaction. In this case, the second stage may follow on immediately from the first. Alternatively, the second stage may be commenced only

after a certain time, for example, after from 10 minutes to 10 hours.

The amount, and rate of addition, of the initiator is preferably chosen so as to give an acrylate copolymer (A1) having a number-average molecular weight M_n of from 1 000 to 30 000 daltons. It is preferred to commence the addition of initiator some time, generally from about 1 to 15 minutes, before the addition of the monomers. Furthermore, preference is given to a process in which the addition of initiator is commenced at the same point in time as the addition of the monomers and ended about half an hour after the addition of the monomers. The initiator is preferably added in a constant amount per unit time. Following the end of the addition of initiator, the reaction mixture is held at polymerization temperature until (generally 1.5 hours) all of the monomers used have undergone substantially complete reaction. "Substantially complete reaction" is intended to denote that preferably 100% by weight of the monomers used have been reacted but that it is also possible for a small residual monomer content of not more than up to about 0.5% by weight, based on the weight of the reaction mixture, to remain unreacted.

25

Preferably, the monomers for preparing the acrylate copolymers (A1) are polymerized with not too high a polymerization solid, preferably with a polymerization solid of from 80 to 50% by weight, based on the

monomers, and then the solvents are partially removed by distillation, so that the resulting acrylate copolymer solutions (A) have a solids content of preferably from 100 to 60% by weight.

5

For use in the inventive coating material, the solids content of the acrylate copolymer solutions (A) is adjusted with at least one preferably aromatic-free solvent preferably to less than 60% by weight, particularly preferably less than 40% by weight, and in particular less than 30% by weight.

Example of suitable solvents are ethoxyethyl propionate and butyl glycol.

15

The preparation of the acrylate copolymers (A1) for inventive use has no special features in terms of method but instead takes place with the aid of the methods which are customary and known in the field of polymers for continuous or batchwise copolymerization under atmospheric or superatmospheric pressure in stirred tanks, autoclaves, tube reactors or Taylor reactors.

25 Examples of suitable copolymerization processes are described in the patents DE-A-197 09 465, DE-C-197 09 476, DE-A-28 48 906, DE-A-195 24 182, EP-A-0 554 783, WO 95/27742 or WO 82/02387.

In accordance with the invention, Taylor reactors are advantageous.

Taylor reactors, which serve to convert substances
5 under the conditions of Taylor vortex flow, are known.
They consist essentially of two coaxial concentric
cylinders of which the outer is fixed while the inner
rotates. The reaction space is the volume formed by the
gap between the cylinders. Increasing angular velocity
10 ω_i of the inner cylinder is accompanied by a series of
different flow patterns which are characterized by a
dimensionless parameter, known as the Taylor number Ta.
As well as the angular velocity of the stirrer, the
Taylor number is also dependent on the kinematic
15 viscosity ν of the fluid in the gap and on the
geometric parameters, the external radius of the inner
cylinder r_i , the internal radius of the outer cylinder
 r_o and the gap width d , the difference between the two
radii, in accordance with the following formula:

20

$$Ta = \omega_i r_i d \nu^{-1} (d/r_i)^{1/2} \quad (I)$$

where $d = r_o - r_i$.

At low angular velocity, the laminar Couette flow, a
25 simple shear flow, develops. If the rotary speed of the
inner cylinder is increased further, then, above a
critical level, alternately contrarotating vortices
(rotating in opposition) occur, with axes along the
peripheral direction. These vortices, called Taylor

vortices, are rotationally symmetric and have a diameter which is approximately the same size as the gap width. Two adjacent vortices form a vortex pair or a vortex cell.

5

The basis of this behavior is the fact that, in the course of rotation of the inner cylinder with the outer cylinder at rest, the fluid particles that are near to the inner cylinder are subject to a greater centrifugal force than those at a greater distance from the inner cylinder. This difference in the acting centrifugal forces displaces the fluid particles from the inner to the outer cylinder. The centrifugal force acts counter to the viscosity force, since for the motion of the fluid particles it is necessary to overcome the friction. If there is an increase in the rotary speed, there is also an increase in the centrifugal force. The Taylor vortices are formed when the centrifugal force exceeds the stabilizing viscosity force.

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In the case of Taylor flow with a low axial flow, each vortex pair passes through the gap, with only a low level of mass transfer between adjacent vortex pairs. Mixing within such vortex pairs is very high, whereas axial mixing beyond the pair boundaries is very low. A vortex pair may therefore be regarded as a stirred tank in which there is thorough mixing. Consequently, the flow system behaves as an ideal flow tube in that the

vortex pairs pass through the gap with constant residence time, like ideal stirred tanks.

Of advantage in accordance with the invention here are

5 Taylor reactors having an external reactor wall located within which there is a concentrically or eccentrically disposed rotor, a reactor floor and a reactor lid, which together define the annular reactor volume, at least one means for metered addition of reactants, and

10 a means for the discharge of product, where the reactor wall and/or the rotor are or is geometrically designed in such a way that the conditions for Taylor vortex flow are met over substantially the entire reactor length in the reactor volume, i.e. in such a way that

15 the annular gap broadens in the direction of flow traversal.

The proportion of the constituent (A) in the coating material of the invention may vary very widely and is

20 guided in particular by the intended flexibility of the inventive sol-gel coating produced therefrom. There is an upper limit on the proportion; thus, it may not be chosen so high that phase separation occurs in the coating material of the invention, or the hardness and

25 scratch resistance of the sol-gel coating decrease too sharply. The skilled worker is therefore able to determine the proportion which is optimal in each case, on the basis of his or her knowledge in the art, with or without the assistance of simple preliminary tests.

The further essential constituent of the coating material of the invention is the stock varnish (B). It too is preferably free of aromatic solvents.

- 5 It is prepared by controlled hydrolysis and condensation of at least one organically modified hydrolyzable silane (B1). In accordance with the invention it is of advantage to use at least two silanes (B1).
- 10 The hydrolyzable silane (B1) comprises compounds of the general formula I



- 15 in which the radicals R may be identical or different and are selected from hydrolyzable groups, hydroxyl groups, and nonhydrolyzable groups.

- The nonhydrolyzable groups R in the general formula (I)
- 20 are preferably selected from alkyl groups, having in particular 1 to 4 carbon atoms, such as methyl, ethyl, propyl and butyl groups; alkenyl groups, having in particular 2 to 4 carbon atoms, such as vinyl, 1-propenyl, 2-propenyl and butenyl groups; alkynyl
- 25 groups, having in particular 2 to 4 carbon atoms, such as acetylenyl and propargyl groups; and aryl groups, having in particular 6 to 10 carbon atoms, such as phenyl and naphthyl groups, for example. Nonhydrolyzable groups R used are preferably alkyl groups.

Examples of hydrolyzable groups R in the above formula I are hydrogen atoms; alkoxy groups, having in particular 1 to 20 carbon atoms, such as methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, tert-butoxy and 5 sec-butoxy groups; alkoxy-substituted alkoxy groups, such as beta-methoxyethoxy groups; acyloxy groups, having in particular 1 to 4 carbon atoms, such as acetoxym and propionyloxy groups; and alkylcarbonyl groups such as acetyl groups, for example.

10

Particularly preferred hydrolyzable groups R are those which carry no substituents and lead to aromatics-free hydrolysis products of low molecular weight, examples being lower alcohols, such as methanol, ethanol, 15 propanol, n-butanol, i-butanol, sec-butanol, and tert-butanol.

At least one group R of the formula I must be a hydrolyzable group. Silanes (B1) having two, preferably 20 and four in particular three hydrolyzable groups R are particularly preferred.

The nonhydrolyzable groups R of the silanes (B1) may include at least one functional group. These functional 25 groups can, for example, be epoxy groups, amino groups, olefinically unsaturated groups such as vinyl or (meth)acrylic groups, mercapto groups, isocyanate groups and/or reaction products thereof with further reactive compounds.

Examples of highly suitable hydrolyzable silanes (B1) for use in accordance with the invention are methyltriethoxysilane, methyltrimethoxysilane, tetramethyl orthosilicate, tetraethyl orthosilicate, 5 3-glycidyloxypropyltrimethoxysilane, and 3-aminopropyltriethoxysilane.

The silanes (B1) can be used in whole or in part in the form of precondensates, i.e., compounds formed by 10 partial hydrolysis of the silanes (B1), either alone or in a mixture with other hydrolyzable compounds.

For the hydrolysis and condensation, the silanes (B1) are precondensed in the desired proportion with water. 15 The amount of water is metered in in such a way as to avoid local excess concentrations. This is done, for example, by introducing the amount of water into the reaction mixture using moisture-laden adsorbents, e.g., silica gel or molecular sieves, hydrous organic 20 solvents, e.g., 80% ethanol, or salt hydrates, e.g., $\text{CaCl}_2 \times 6\text{H}_2\text{O}$. Precondensation takes place preferably in the presence of a hydrolysis and condensation catalyst but in the absence of an organic solvent.

25 In another variant, the hydrolysis and condensation of the hydrolyzable silanes (B1) is conducted in the presence of a preferably aromatics-free organic solvent, such as an aliphatic alcohol, such as methanol, ethanol, propanol, isopropanol or butanol, an

ether such as dimethoxyethane, an ester such as dimethyl glycol acetate or methoxypropyl acetate, and/or 2-ethoxyethanol (ethyl glycol) or a ketone such as acetone or methyl ethyl ketone.

5

If desired, metal compounds and/or metal oxides in the form of nanoparticles may also be present during the hydrolysis and condensation.

10 These nanoparticles are < 50 nm. They may comprise, for example, Al_2O_3 , ZrO_2 and/or TiO_2 .

Examples of suitable metal compounds are hydrolyzable metal compounds (B2) of the general formula (II)

15



In the general formula II, the variable M stands for aluminum, titanium or zirconium, but especially
20 aluminum. Accordingly, the index n stands for 3 or 4.

In the general formula II, the variable R has the same definition as indicated above in connection with the general formula I. It is of advantage here if in the
25 case of aluminum there are at least two, in particular three, and in the case of titanium or zirconium there are three, in particular four, hydrolyzable groups present.

In this context, the above-described alkoxy groups are particularly advantageous and are therefore used with preference. Very particular preference is given to using sec-butyloxy groups. One example of a very
5 particularly preferably used hydrolyzable metal compound (B2) is therefore aluminum tri-sec-butylate.

The molar ratio of metal M to silicon may vary widely and is guided in particular by the target scratch
10 resistance and hardness of the sol-gel coatings of the invention. In general, the scratch resistance of the sol-gel coatings of the invention may be increased by replacing some of the silicon with - in particular - aluminum. In particular, the molar ratio M : Si may be
15 from 1 : 10 to 10 : 1.5, preferably from 1 : 6 to 1 : 3.

Suitable hydrolysis and condensation catalysts include proton- or hydroxyl-ion-donating compounds and amines.
20 Specific examples are organic or inorganic acids, such as hydrochloric acid, sulfuric acid, phosphoric acid, formic acid or acetic acid, and organic or inorganic bases such as ammonia, alkali metal hydroxides or alkaline earth metal hydroxides, e.g., sodium,
25 potassium or calcium hydroxide, and amines soluble in the reaction medium, examples being lower alkylamines or alkanolamines. Particular preference is given in this context to volatile acids and bases, especially

hydrochloric acid, acetic acid, ammonia or triethylamine.

The precondensation is continued until the resulting
5 stock varnish (B) still has a liquid consistency. Preferably, it has a solids content of less than 80% by weight, with particular preference less than 60% by weight, and in particular less than 40% by weight.

- 10 The fraction of the constituent (B) in the coating material of the invention may also vary very widely and is guided in particular by the target scratch resistance and hardness of the sol-gel coating of the invention which is produced from said coating material.
- 15 There is an upper limit on the fraction; thus, it may not be chosen so high that there is phase separation in the coating material of the invention and/or that the sol-gel coatings of the invention produced using it become too hard and brittle. The skilled worker will
- 20 therefore be able to determine the fraction that is optimum in each case, on the basis of his or her knowledge of the art, with or without the assistance of simple preliminary tests.
- 25 The third essential constituent of the coating material of the invention is the additive solution (C).

This solution comprises at least one ethylenically unsaturated compound (c1) containing at least one

epoxide group. An example of a suitable compound (c1) is glycidyl (meth)acrylate.

It further comprises as component (c2) at least one
5 silane (B1) containing at least one nonhydrolyzable group R which contains at least one epoxide group. An example of a suitable compound (c2) is 3-glycidyloxypropyltrimethoxysilane.

10 Not least, it comprises at least one adduct (c3) of at least one silane (B1) containing at least one nonhydrolyzable group R having at least one amino group, and at least one cyclic, ethylenically unsaturated dicarboxylic anhydride. An example of a suitable silane
15 (B1) is 3-aminopropyltriethoxysilane. Examples of suitable dicarboxylic anhydrides are maleic anhydride and itaconic anhydride.

The additive solution contains the components (c1),
20 (c2) and (c3) in a weight ratio of (1 to 10):(1 to 30):1, in particular (2 to 6):(10 to 20):1. The solids content of the additive solution (C) is preferably below 80% by weight, more preferably below 60% by weight, and in particular below 50% by weight.

25

The proportion of the additive solution (C) in the coating material of the invention may also vary widely. The skilled worker is able to determine the proportion that is optimal in each case, on the basis of his or

her knowledge in the art, with or without the assistance of simple preliminary tests.

Particularly advantageous coating materials of the invention contain, based in each case on their overall amount, from 5 to 20, preferably from 10 to 15, and in particular from 11 to 14% by weight of the acrylate copolymer solution (A), from 40 to 85, preferably from 45 to 80, and in particular from 50 to 75% by weight of the stock varnish (B), and from 0.5 to 3, preferably from 1 to 2, and in particular from 1.2 to 1.7% by weight of the additive solution (C).

It is of very particular advantage in this context, in accordance with the invention, for the solids contents of the constituents (A), (B) and (C) that are essential to the invention to be chosen such that their mutual weight ratio (A) : (B) : (C) is

- 20 - 1 to 10:30 to 60:1
- preferably 2 to 8:35 to 55:1, and
- especially 2.5 to 6:40 to 50:1.

25

The coating material of the invention may further comprise at least one curing agent (D). Examples of suitable curing agents (D) are quaternary ammonium compounds such as tetraalkylammonium salts, especially

tetramethylammonium iodide. In the coating material of the invention, the curing agent (D) may preferably be present in an amount of from 0.001 to 1% by weight.

5 The coating material of the invention may further comprise relatively large amounts of preferably non-aromatic solvents as constituent (E). This is particularly the case when particularly thin sol-gel coatings of the invention are to be produced. Examples
10 of suitable solvents (E) are the abovementioned lower alcohols, especially ethanol, or glycol ethers such as ethyl glycol or butyl glycol.

The coating material of the invention may further
15 comprise customary and known coatings additives (F). Suitable coatings additives (F) are all those which do not adversely effect, but instead advantageously vary and enhance, the profile of properties of the sol-gel coatings of the invention, especially their optical
20 properties (appearance) and scratch resistance.

Examples of suitable coatings additives (F) are

- light stabilizers such as UV absorbers;
- 25 - free-radical scavengers;
- crosslinking catalysts;

- slip additives;
- polymerization inhibitors;
- 5 - defoamers;
- emulsifiers, especially nonionic emulsifiers such as alkoxyated alkanols and polyols, phenols and alkylphenols or anionic emulsifiers such as alkali metal salts or ammonium salts of alkanecarboxylic acids, alkanesulfonic acids, and sulfonic acids of alkoxyated alkanols and polyols, phenols and alkylphenols;
- 10 - wetting agents such as siloxanes, fluorine compounds, carboxylic monoesters, phosphoric esters, polyacrylic acids and their copolymers, or polyurethanes;
- 15 - adhesion promoters;
- leveling agents;
- film-forming auxiliaries such as cellulose derivatives;
- 25 - flame retardants or

- rheology control additives such as those known from the patents WO 94/22968, EP-A-0 276 501, EP-A-0 249 201 or WO 97/12945; crosslinked polymeric microparticles, such as are disclosed, for example, in EP-A-0 008 127; inorganic phyllosilicates such as aluminum magnesium silicates, sodium magnesium phyllosilicates and sodium magnesium fluorine lithium phyllosilicates of the montmorillonite type; silicas such as Aerosils; or synthetic polymers containing ionic and/or associative groups such as polyvinyl alcohol, poly(meth)acrylamide, poly(meth)acrylic acid, polyvinylpyrrolidone, styrene-maleic anhydride copolymers or ethylene maleic anhydride copolymers and their derivatives or hydrophobically modified ethoxylated urethanes or polyacrylates.

Further examples of suitable additives (E) are described in the textbook "Lackadditive" [Additives for Coatings] by Johan Bieleman, Wiley-VCH, Weinheim, New York, 1998.

The coating material of the invention has a solids content of up to 80, preferably up to 60, with particular preference up to 40, and in particular up to 20, % by weight. Where particularly thin sol-gel coatings of the invention, i.e., coatings with a thickness $< 5 \mu\text{m}$, are to be produced, it is advisable to choose a solids content of less than 20% by weight.

5 The preparation of the coating material of the invention has no special features but instead takes place in a customary and known manner by mixing of its essential constituents (A), (B) and (C) and also, where used, (D), (E) and/or (F) in customary and known mixing units such as dissolvers. The constituents here may be mixed with one another in any desired way. For example, they may be introduced all at once into the mixing unit and mixed with one another. In accordance with the invention, however, it is of advantage to introduce the stock varnish (B) initially and then to add the remaining constituents individually in succession. It has been found appropriate here to add the acrylate copolymer solution (A) before the additive solution (C). Where a solvent (E) is used, it is advantageously added following the addition of the acrylate copolymer solution (A) and before the addition of the additive solution (C). Where coatings additives (F) are used, they are added advantageously following the addition of the acrylate copolymer solution (A). The curing agent (D) is advantageously added last.

25 The coating materials of the invention are outstandingly suitable for the production of the sol-gel coatings of the invention, especially sol-gel clearcoats.

In accordance with the invention, they can be used to coat any conceivable substrate. By way of example,

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materials of the invention advantageously in automotive
refinish. Since it is also possible in this context to
restrict to a minimum the amount of the coating
material of the invention, its use is also particularly
5 economical.

The coating materials of the invention may be applied
directly to the abovementioned primed or unprimed
substrates in order to form thereon, after curing, a
10 scratch-proof sol-gel coating of the invention. In this
way it is possible to scratchproof substrates such as
are commonly used for the production of vehicles, of
other components and equipment, such as radiators or
containers, or of furniture.

15 The particular advantages of the coating materials of
the invention are manifested to a particular extent,
however, if they are used for the coating of single-
coat or multicoat paint systems with the sol-gel
20 coatings of the invention.

Accordingly, the coating materials of the invention are
suitable for coating single-coat or multicoat paint
systems, especially single-coat or multicoat color
25 and/or effect paint systems such as are customary and
known in the fields of automotive OEM finishing,
automotive refinish, industrial coating, including
container coatings, the coating of plastics, and
furniture coating.

Examples of single-coat paint systems of this kind are the solid-color topcoats described at the outset and known from automotive OEM finishing and automotive refinish, especially those based on the two-component
5 (2K) solid-color topcoat materials, or clear, transparent paint systems based on the clearcoat materials described below, especially the one-component (1K) clearcoat materials, the two-component (2K) or multicomponent (3K, 4K) clearcoat materials, the powder
10 clearcoat materials and the UV-curable clearcoat materials.

Examples of multicoat paint systems are the paint systems which comprise an effect and/or color basecoat,
15 especially one based on an aqueous basecoat material, and a clearcoat, particularly one based on a one-component (1K) clearcoat material, two-component (2K) or multicomponent (3K, 4K) clearcoat material, powder clearcoat material, powder slurry clearcoat material or
20 UV-curable clearcoat material, in particular a two-component (2K) or multicomponent (3K, 4K) clearcoat material, and which are produced in the context of automotive OEM finishing by the wet-on-wet technique or in the context of automotive refinish.

25

The coating materials of the invention are particularly outstandingly suitable for coating multicoat paint systems of this kind in particular.

Examples of suitable aqueous basecoat materials and of the corresponding multicoat paint systems are known from the patents EP-A-0 089 497, EP-A-0 256 540, EP-A-0 260 447, EP-A-0 297 576, WO 96/12747, EP-A-0 523 610, 5 EP-A-0 228 003, EP-A-0 397 806, EP-A-0 574 417, EP-A-0 574 510, EP-A-0 581 211, EP-A-0 708 788, EP-A-0 593 454, DE-A-43 28 092, EP-A-0 299 148, EP-A-0 394 737, EP-A-0 590 484, EP-A-0 234 362, EP-A-0 234 361, EP-A-0 543 817, WO 95/14721, EP-A-0 521 928, EP-A-0 522 420, EP-A-10 0 522 419, EP-A-0 649 865, EP-A-0 536 712, EP-A-0 596 460, EP-A-0 596 461, EP-A-0 584 818, EP-A-0 669 356, EP-A-0 634 431, EP-A-0 678 536, EP-A-0 354 261, EP-A-0 424 705, WO 97/49745, WO 97/49747 or EP-A-0 401 565.

15 When two-component (2K) solid-color topcoat materials or one-component (1K) clearcoat materials, two-component (2K) or multicomponent (3K, 4K) clearcoat materials, powder clearcoat materials and UV-curable clearcoat materials, especially two-component (2K) or 20 multicomponent (3K, 4K) clearcoat materials, are used to produce single-coat or multicoat paint systems, there is the further key advantage that the sol-gel coatings can be suitably produced using not only the coating materials of the invention but also conventional 25 sol-gel clearcoat materials, if the said coating materials are partly cured following their application and before the application of the sol-gel clearcoat materials. After this, the said coating materials are cured completely together with the sol-gel clearcoat

materials. This inventive procedure results in particularly good adhesion between the coating films and the sol-gel coatings. Particularly outstanding results are obtained if the coating materials of the invention are
5 used in the process of the invention.

Examples of suitable one-component (1K), two-component (2K) or multicomponent (3K, 4K) clearcoat materials are known, for example, from the patents DE-A-42 04 518,
10 US-A-5,474,811, US-A-5,356,669, US-A-5,605,965, WO 94/10211, WO 95/10212, WO 94/10213, EP-A-0 594 068, EP-A-0 594 071, EP-A-0 594 142, EP-A-0 604 992, WO 94/22969, EP-A-0 596 460 or WO 92/22615.

15 One-component (1K) clearcoat materials comprise, as is known, hydroxyl-containing binders and crosslinking agents such as blocked polyisocyanates, tris(alkoxy-carbonylamino)triazines and/or amino resins. In a further variant, they comprise as binders polymers
20 containing pendant carbamate and/or allophanate groups and, if desired, carbamate- and/or allophanate-modified amino resins as crosslinking agents.

Two-component (2K) or multicomponent (3K, 4K) clearcoat
25 materials contain, as is known, the essential constituents hydroxyl-containing binders and polyisocyanate crosslinking agents, these constituents being stored separately until such time as they are used.

Examples of suitable powder clearcoat materials are known, for example, from the German patent DE-A-42 22 194 or the BASF Lacke + Farben AG product information bulletin "Pulverlacke" [Powder coating materials], 1990.

Powder clearcoat materials are known to contain as their essential constituents binders containing epoxide groups and polycarboxylic acid crosslinking agents.

10

Examples of suitable powder slurry clearcoat materials are known, for example, from the U.S. patent US-A-4,268,542 and the German patent applications DE-A-195 18 392.4 and DE-A-196 13 547 or are described in the German patent application DE-A-198 14 471.7, unpublished at the priority date of the present specification.

Powder slurry clearcoat materials are known to comprise powder clearcoat materials in dispersion in an aqueous medium.

UV-curable clearcoat materials are disclosed, for example, by the patents EP-A-0 540 884, EP-A-0 568 967 or US-A-4,675,234.

Their familiar components are low molecular mass, oligomeric and/or polymeric compounds curable with actinic light and/or electron beams, preferably

radiation-curable binders, based in particular on ethylenically unsaturated prepolymers and/or ethylenically unsaturated oligomers, one or more reactive diluents, if desired, and one or more photoinitiators, 5 if desired. Examples of suitable radiation-curable binders are (meth)acryloyl-functional (meth)acrylic copolymers, polyether acrylates, polyester acrylates, unsaturated polyesters, epoxy acrylates, urethane acrylates, amino acrylates, melamine acrylates, 10 silicone acrylates, and the corresponding methacrylates. Preference is given to using binders which are free of aromatic structural units.

It is, however, also possible to employ multicoat 15 clearcoats, such as, for instance, a clearcoat based on hydroxyl-containing binders and blocked polyisocyanates and amino resins as crosslinking agents, which lies immediately atop the aqueous basecoat and atop which there is a further clearcoat based on binders 20 containing carbamate and/or allophanate groups and on amino resins as crosslinking agents.

The sol-gel coatings of the invention which are produced preferably by the process of the invention 25 from the coating materials of the invention are notable for outstanding scratch resistance coupled with very good adhesion, even following exposure to condensation. The appearance is also very good. The process of the invention is therefore suitable in particular for the

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painting of vehicle bodies, especially of automobile bodies, with multicoat paint systems, for industrial coating, including container coatings, and for furniture coating.

5

Examples

Preparation example

10 **The preparation of the inventive sol-gel clearcoat material**

1. The preparation of a stock varnish

15 A suitable reaction vessel was charged under nitrogen with 30 parts of fully deionized water, 40 parts of ethyl glycol, 5 parts of acetic acid (100% strength), 66.5 parts of methyltriethoxysilane and 4.7 parts of 3-glycidyloxypropyltrimethoxysilane and this initial
20 charge was heated with stirring to 60°C. After a further 3 hours at 60°C, the reaction mixture was heated with stirring to 90°C and held at this temperature for 2 hours more. Thereafter, 70 parts of the reaction mixture were distilled off azeotropically at
25 85°C. After the reaction mixture had been cooled to room temperature, 5 parts of methoxypropyl acetate and 0.1 part of BYK® 301 (leveling agent from BYK) were added to it. This gave the stock varnish 1, having a theoretical solids content of 37% by weight and an

experimentally determined solids content of 46.9% by weight (1 hour/130°C). For the preparation of a sol-gel clearcoat material 4b, the solid was adjusted to 40.3% by weight.

5

2. The preparation of an acrylate copolymer for modifying the sol-gel clearcoat material (solution for organic modification 2)

10 An appropriate stirring vessel with reflux condenser and stirring was charged with 39 parts of ethoxyethyl propionate and this initial charge was heated to 130°C. In a first monomer feed vessel, a premix was formed from 9.598 parts of butyl methacrylate, 7.708 parts of methyl methacrylate, 8.003 parts of styrene, 4.253 parts of Methacrylester 13.0 (methacrylic ester with a long alkyl radical in the ester moiety) and 9.096 parts of hydroxyethyl acrylate. A second monomer feed vessel was charged with 3.810 parts of hydroxyethyl acrylate, 1.831 parts of acrylic acid and 0.916 part of ethoxyethyl propionate. An initiator feed vessel was charged with 3.692 parts of peroxide TBPEH (tert-butyl perethylhexanoate) and 6.025 parts of ethoxyethyl propionate. The contents of the first monomer feed vessel were metered into the reactor at a uniform rate over the course of four hours. After two hours and 30 minutes following the beginning of the first monomer feed, the second monomer feed was commenced. For this purpose, the contents of the second

monomer feed vessel were metered into the reactor at a uniform rate over the course of one hour and 30 minutes. The contents of the initiator feed vessel were metered into the reactor at a uniform rate over the course of four hours and 30 minutes, the initiator feed being commenced five minutes before the first monomer feed. After the end of the feeds, the resulting reaction mixture was polymerized at 130°C for two hours until an original viscosity of 2.2 dPas, a solids content of 50% by weight (15 minutes/180°C) and an acid number of 30 mg KOH/g had been reached. Thereafter, the ethoxyethyl propionate was distilled off in vacuo at 100°C until a solids content of 81% by weight (15 minutes/180°C) had been reached. The resulting reaction mixture was cooled to 80°C and adjusted with butyl glycol and ethoxyethyl propionate (weight ratio 5 : 1) to a solids content of 75% by weight.

For the preparation of the inventive sol-gel clearcoat material, the solution of the acrylate copolymer was adjusted with butyl glycol to a solids content of 20% by weight, to give the solution for organic modification 2.

3. The preparation of an additive solution

15 parts of ethyl glycol, 2 parts of 2,3-epoxypropyl methacrylate (glycidyl methacrylate), 7.5 parts of 3-glycidyloxypropyltrimethoxysilane, 0.5 part of an

adduct of maleic anhydride and 3-aminopropyltriethoxy-
silane, and 0.1 part of azodicarboxamide (GenitronR
AZDN - M) were mixed with one another at 100°C, with
stirring, for six hours. This gave the additive
5 solution 3, having an experimentally determined solids
content of 40% by weight (15 minutes/180°C).

The adduct itself was prepared by reacting 220 parts of
3-aminopropyltriethoxysilane and 100 parts of maleic
10 anhydride with one another.

4. The preparation of the inventive sol-gel clearcoat materials 4a and 4b

15 4.1 The sol-gel clearcoat material 4a

The sol-gel clearcoat material 4a was obtained by
mixing in, with stirring and in succession, 14.77 parts
of the solution for organic modification 2, 20.8 parts
20 of methoxypropyl acetate, 0.014 part of BYK® 301,
1.57 parts of the additive solution 3, 0.8 part of
Tinuvin® 384 and 0.6 part of Tinuvin® 123 (light
stabilizers from Ciba-Geigy) with one another to
61.2 parts of the stock varnish 4 (46.9% strength by
25 weight in ethyl glycol). To the resulting mixture there
were added 7.0 parts of tetramethylammonium iodide
solution (3% strength in 1 : 1 methanol/water). The
resulting sol-gel clearcoat material 4a was stirred at
room temperature for 30 minutes. It had a solids

content of 32% by weight (15 minutes/180°C). The sol-gel clearcoat material 4a was used to produce a sol-gel coating on a single-coat paint system based on a two-component (2K) solid-color topcoat material (example 5 1).

4.2 The sol-gel clearcoat material 4b

The sol-gel clearcoat material 4b was obtained by 10 adding, with stirring and in succession, 11.77 parts of the solution for organic modification 2, 14.89 parts of methoxypropyl acetate, 0.47 part of BYK® 301 and 1.57 parts of the additive solution 3 to 71.3 parts of the stock varnish 4 (40.3% strength by weight in ethyl 15 glycol). The resulting sol-gel clearcoat material 4b was used to produce a sol-gel coating on a multicoat paint system with a clearcoat based on a commercially customary two-component (2K) clearcoat material (example 2).

20

Example 1

The production of an inventive sol-gel coating on a single-coat paint system

25

Steel panels coated cathodically with a commercially customary electrocoat material (electrodeposition coating with a film thickness of 18 - 22 μm) were first of all coated, using a cup-type gun, with a commercial

primer-surfacer from BASF Coatings AG, and then baked. This gave a primer-surfacer coat having a film thickness of from 35 to 40 μm . Atop the primer-surfacer coat there was applied a commercial two-component (2K) solid-color topcoat material (AK66-1110 Ral 9005 Schwarz (black) from BASF Coatings AG), and initial drying and partial curing took place at 50°C over 15 minutes.

10 After the panels had cooled, the sol-gel clearcoat material 4a was applied. Thereafter, the solid-color topcoat film and the sol-gel clearcoat film were cured together at 90°C for 4 hours.

15 This gave a paint system having a solid-color topcoat with a thickness of 45 μm and the inventive sol-gel coating with a thickness of 8 μm . The paint system was free from cracks and gave a very good overall visual impression.

20

Example 2

The production of an inventive sol-gel coating on a multicoat paint system

25

Steel panels coated cathodically with a commercially customary electrocoat material (electrodeposition coating with a film thickness of 18 - 22 μm) were first of all coated, using a cup-type gun, with a commercial

primer-surfacer from BASF Coatings AG, and then baked. This gave a primer-surfacer coat having a film thickness of from 35 to 40 μm . Thereafter, a green aqueous metallic basecoat material (Ecostar^R Dschungelgrün [jungle green] from BASF Coatings AG) was applied to the primer-surfacer in the same way and was initially dried at 80°C for 10 minutes. After the panels had cooled, a film of a commercial two-component (2K) clearcoat material (FF95-0111 from BASF Coatings AG) was applied and was initially dried and partially cured at 80°C for 10 minutes.

After the coated panels had cooled, the inventive sol-gel clearcoat material 4b in accordance with the preparation example was applied. The aqueous basecoat film, the clearcoat film, and the sol-gel clearcoat film were subsequently cured together at 150°C over 30 minutes.

This gave a multicoat paint system comprising a basecoat with a thickness of 15 μm , a clearcoat with a thickness of 44 μm , and the inventive sol-gel coating, with a thickness of 8 μm . The paint system was free from cracks and gave a very good overall visual impression.

Example 3

The testing of the properties of the inventive sol-gel coatings of examples 1 and 2

5

3.1 Adhesion of the sol-gel coating

Table 1 gives an overview of the tests conducted and the results obtained in those tests.

10

Table 1:**Adhesive strength of the inventive sol-gel coatings**

Test methods	Example	
	1	2
Scratch trial to DBL 7399 [rating 0 to 5]	0	0
Scratch trial after 240 hours of constant condensation conditioning [CCC] [rating 0 to 5]	0	0
Cross-hatch to DIN 53151 (2 mm) [rating 0 to 5]	0	0
Cross-hatch after 240 hours of CCC and 24 hours of regeneration	0	0

15 [Rating 0 to 5]: 0 = best score; 5 = worst score

The results of table 1 demonstrate the outstanding adhesion of the inventive sol-gel coatings to the respective paint systems.

5 3.2 The scratch resistance of the sol-gel coating

3.2.1 By the brush test

For this test, the test panels were stored at room
10 temperature for at least 2 weeks following application
of the coating materials, before the test was
conducted.

The scratch resistance of the sol-gel coating on the
15 test panels was assessed using the BASF brush test
described in fig. 2 on page 28 of the article by P. Betz
and A. Bartelt, Progress in Organic Coatings, 22 (1993),
pages 27 - 37, albeit with modification in respect of
the weight used (2 000 g instead of the 280 g specified
20 therein), assessment taking place as follows:

In the test, the paint surface was damaged with a woven
mesh which was loaded with a weight. The woven mesh and
the paint surface were wetted copiously with a laundry
25 detergent solution. The test panel was moved backward
and forward under the woven mesh in reciprocating
movements, by means of a motor drive.

The test element was an eraser (4.5 × 2.0 cm, broad side perpendicular to the direction of scratching) around which there was scratched a woven nylon mesh (No. 11, 31 μm mesh size, Tg 50°C). The applied weight
5 was 2 000 g.

Prior to each test, the woven mesh was replaced, with the running direction of the woven meshes parallel to the direction of scratching. Using a pipette, about
10 1 ml of a freshly stirred 0.25% Persil solution was applied in front of the eraser. The speed of rotation of the motor was set so as to perform 80 double strokes within a period of 80 s. After the test, the remaining detergent liquid was rinsed off with cold tap water and
15 the test panel was blown dry with compressed air. Here, it became evident that the inventive sol-gel coatings had not been scratched away at all.

3.2.2 By the sand test

20

In addition, the scratch resistance was determined by the sand test. For this purpose, the paint surfaces were loaded with sand (20 g of quartz silver sand, 1.5-2.0 mm). The sand was placed in a beaker (with its base
25 cut off in a planar fashion) which was firmly fastened on the test panel. The test panels used were the same as those described above in the brush test. Using a motor drive, the panel with the beaker and the sand was set in shaking movements. The movement of the loose

sand caused damage to the paint surface (100 double strokes in 20 s). Following sand exposure, the test area was cleaned to remove abraded material, wiped off carefully under a jet of cold water, and then dried
5 using compressed air. Measurements were made of the gloss to DIN 67530 before and after damage.

Here it was found that, as a result of the exposure, the gloss

10

- fell by only 9 gloss units in the case of example 1 and

- by only 13 gloss units in the case of example 2,

15

which is a further demonstration of the extremely high scratch resistance of the inventive sol-gel coating.

3.3.3 By Amtec

20

The scratch resistance was also determined in accordance with Amtec in the case of example 1. Here, the exposure produced a reduction in gloss by only 5 gloss units from the initial figure of 68, which further under-
25 scores the high scratch resistance of the inventive sol-gel coating.

3.4 Chemical resistance

3.4.1 Chemical resistance by the MB gradient oven test

5 For the MB gradient oven test, which is well known to
the skilled worker, the test panels of examples 1 and 2
were subjected in a defined manner to damage by
sulfuric acid, water, pancreatin and tree resin. For
this purpose, the sample substances were applied with a
10 spacing of one segment width in each case (setting of
the gradient to 30 - 75°C [1°C per heating segment]).
Following storage under standard climatic conditions at
23°C for 72 hours, the test panels were exposed in a
gradient oven (e.g., type: 2615 from BYK-Gardner) for
15 30 minutes. A determination was made of the temperature
at which the first visible change occurred.

The results of testing are given in table 2.

20 **Table 2: Chemical resistance by the MB gradient oven test**

Test substance	Example 1	Example 2
	1st marking at °C	1st marking at °C
1% strength sulfuric acid	61	55
Distilled water	> 75	> 75
Pancreatin	< 50	< 50
Tree resin	> 75	> 75

The results of the MB gradient oven test underscore the high chemical resistance of the inventive sol-gel coating.

5 **3.4.2 By the MEK test**

The solvent resistance of the inventive sol-gel coatings of examples 1 and 2 were tested in accordance with the provisions of the MEK test, which is well
10 known to the skilled worker. Even after 200 double strokes with cotton pads soaked with methyl ethyl ketone, no instances of damage were evident.

15 **3.5 Stone chipping test**

The VDA [German Automakers' Association] stone chipping test with multi-impact exposure (2 × 500 grams/2 bar), which is known to those skilled in the art, gave a characteristic value of 3 and a rusting degree of 2 for
20 both examples, 1 and 2. Accordingly, the inventive sol-gel coating together with the single-coat (example 1) and the multicoat (example 2) paint system, proved sufficiently stable with respect to stone chipping.

25 **3.6 Erichsen indentation**

The Erichsen indentation to DIN EN ISO 1520: 1995-04 was 0.5 mm (example 1) and 0.4 mm (example 2).

Claims

1. A sol-gel coating material comprising

- 5 (A) an acrylate copolymer solution comprising at least one acrylate copolymer (A1) preparable by copolymerizing at least the following monomers:
- 10 a1) at least one (meth)acrylic ester which is substantially free of acid groups,
- a2) at least one ethylenically unsaturated monomer which carries at least one
- 15 hydroxyl group per molecule and is substantially free of acid groups, and
- a3) at least one ethylenically unsaturated monomer which carries per molecule at
- 20 least one acid group which can be converted into the corresponding acid anion group;
- (B) a stock varnish preparable by hydrolyzing and
- 25 condensing at least one hydrolyzable silane (B1) of the general formula I



in which the variable R has the following definition:

R = hydrolyzable groups, hydroxy groups and nonhydrolyzable groups, with the proviso that at least one, preferably at least two, hydrolyzable group(s) is or are present;

10 and

(C) an additive solution comprising

15 c1) at least one ethylenically unsaturated compound containing at least one epoxide group,

20 c2) at least one silane (B1) having at least one nonhydrolyzable group R which contains at least one epoxide group, and

25 c3) at least one adduct of at least one silane (B1) having at least one nonhydrolyzable group R which contains at least one amino group and at least one cyclic ethylenically unsaturated dicarboxylic anhydride.

2. The sol-gel coating material of claim 1, characterized in that it comprises, based in each case on its overall amount, from 5 to 20, preferably from 10 to 15 and in particular from 11 to 14% by weight of the acrylate copolymer solution (A), from 40 to 85, preferably from 45 to 80, and in particular from 50 to 75% by weight of the stock varnish (B), and from 0.5 to 3, preferably from 1 to 2, and in particular from 1.2 to 1.7% by weight of the additive solution (C).
3. The sol-gel coating material of claim 1 or 2, characterized in that the solids contents of the constituents (A), (B) and (C) are in a weight ratio of (A) : (B) : (C) of
- 1 to 10 : 30 to 60 : 1
 - preferably 2 to 8 : 35 to 55 : 1, and
 - in particular 2.5 to 6 : 40 to 50 : 1.
4. The sol-gel coating material of one of claims 1 to 3, characterized in that the stock varnish (B) comprises at least one hydrolyzable metal compound of the general formula II



in which the variables and the index have the following definition:

M = aluminum, titanium or zirconium,

5

R = hydrolyzable groups, hydroxy groups, and non-hydrolyzable groups, with the proviso that at least one, preferably at least two, hydrolyzable group(s) is or are present, and

10

n = 3 or 4.

5. The sol-gel coating material of one of claims 1 to 4, characterized in that

15

- the nonhydrolyzable groups R are alkyl groups, especially having from 1 to 4 carbon atoms; alkenyl groups, especially having from 2 to 4 carbon atoms; alkynyl groups, especially having from 2 to 4 carbon atoms; and/or aryl groups, especially having from 6 to 10 carbon atoms; and

20

- the hydrolyzable groups R are hydrogen atoms, alkoxy groups, especially having from 1 to 20 carbon atoms; alkoxy-substituted alkoxy groups having from 3 to 20 carbon atoms; acyloxy groups, especially having from 1 to 4

25

carbon atoms; alkylcarbonyl groups,
especially having from 2 to 6 carbon atoms.

5 6. The sol-gel coating material of claim 5, characterized in that

10 - the hydrolyzable groups R are methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, sec-butoxy, beta-methoxyethoxy, acetoxy, propionyloxy and/or acetyl groups and the

15 - the nonhydrolyzable groups R are methyl, ethyl, propyl, butyl vinyl, 1-propenyl, 2-propenyl, butenyl, acetylenyl, propargyl, phenyl and/or and naphthyl groups.

20 7. The sol-gel coating material of one of claims 1 to 6, characterized in that the nonhydrolyzable groups R contain at least one functional group, in particular at least one epoxide group, amino group, olefinically unsaturated group, mercapto group, and/or isocyanate group and/or reaction products thereof with further reactive compounds.

25 8. The sol-gel coating material of one of claims 1 to 7, characterized in that it is a sol-gel clearcoat material.

9. The use of the sol-gel coating material in accordance with one of claims 1 to 8 to produce scratch-resistant sol-gel coatings, especially for single-coat or multicoat paint systems.

5

10. The use of the sol-gel coating material of claim 9, characterized in that the paint systems in question are fully cured single-coat or multi-coat paint systems.

10

11. The use of the sol-gel coating material of claim 9 or 10, characterized in that the paint systems are automotive OEM paint systems, automotive refinish paint systems, industrial paint systems, including container coatings, coatings on plastics and furniture coatings.

15

12. A process for producing scratch-resistant sol-gel coatings by applying and curing sol-gel coating materials on primed or unprimed substrates or unprimed or primed substrates provided with a single-coat or multicoat paint system, characterized in that a sol-gel coating material in accordance with one of claims 1 to 8 is used in this process.

20

25

13. A process for producing scratch-resistant sol-gel coatings by applying and curing sol-gel coating materials on unprimed or primed substrates which

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have been provided with a single-coat or multicoat paint system, characterized in that, prior to the application of the sol-gel coating material,

5 (i1) a single-coat paint system based on a one-component (1K) clearcoat material, two-component (2K) or multicomponent (3K, 4K) clearcoat material, powder clearcoat material or UV-curable clearcoat material,

10

(i2) a multicoat color and/or effect paint system with a topmost coat based on a one-component (1K) clearcoat material, two-component (2K) or multicomponent (3K, 4K) clearcoat material, powder clearcoat material or UV-curable clearcoat material, especially a one-component (1K) clearcoat material, two-component (2K) or multicomponent (3K, 4K) clearcoat material, or

15

20

(i3) a single-coat color and/or effect paint system based on a two-component (2K) solid-color topcoat material

25 is applied and partly cured.

14. The process of claim 13, characterized in that a sol-gel coating material in accordance with one of claims 1 to 8 is used in this process.

15. The process of one of claims 12 to 14, characterized in that the applied sol-gel coating material is cured by exposure to middle-range IR radiation.

5

16. The process of one of claims 12 to 15, characterized in that the paint systems are automotive OEM paint systems, automotive refinish paint systems, industrial paint systems, including container coatings, and furniture coatings.

10

17. Sol-gel coatings which can be produced from a sol-gel coating material in accordance with one of claims 1 to 8 and/or by the process in accordance with one of claims 12 to 16.

15

18. Substrates comprising at least one sol-gel coating
in accordance with claim 17.

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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63) <input type="checkbox"/> Declaration Submitted with initial Filing or <input checked="" type="checkbox"/> Declaration Submitted after initial Filing (surcharge (37 CFR 1.16 (e)) required)	Attorney Docket No.	IN-5513
	First Named Inventor	Peter BETZ et al.
	COMPLETE IF KNOWN	
	Application Number	09/914,937
	Filing Date	September 5, 2001
	Group Art Unit	
	Examiner Name	

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

SOL-GEL COATING FOR SINGLE-LAYER OR MULTI-LAYER VARNISHES

(Title of the Invention)

The specification of which:

☐ is attached hereto

☒ Was filed on **06 March 2000** as United States Application or PCT International Application Number **PCT/EP00/01932** and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application

I hereby claim foreign priority benefits under 35, U.S.C § 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate or 365 (a) of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below, by checking the box, any foreign application(s) for patent or inventor's certificate, or any PCT international application(s) having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date DATE/MONTH/YEAR	Priority Not Claimed	Certified Copy Attached?	
				Yes	No
199 09 894.8	German	6. March 1999	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Additional foreign application number are listed on a supplemental priority data sheet PTO/SB/02B attached hereto:

I hereby claim the benefit under 35 U.S.C 119(e) of any United States provisional application(s) listed below:

APPLICATION NUMBER(S)	FILING DATE	
		<input type="checkbox"/> Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto

DECLARATION —	Utility or Design Patent Application
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

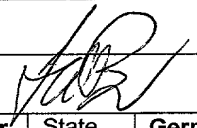
Name OF SOLE OR FIRST INVENTOR:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name Peter (first and middle [if any])				Family Name BETZ or Surname			
Inventor's Signature <i>Peter Betz</i>				Date 30.10.01			
Residence: City	D-48165 Münster	State	Germany	Country	Federal Republic of Germany	Citizenship	German
Mailing Address		Am Roggenkamp 172					
City	D-48165 Münster	State	Germany	Zip			

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Name of Additional Joint Inventor, If any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name (first and middle [if any]) Horst				Family Name or Surname HINTZE-BRÜNING			
Inventor's Signature 				Date 30.10.01			
Residence: City	D-48165 Münster	State	Germany	Country	Federal Republic of Germany	Citizenship	German
Mailing Address		Thomas-Mann-Weg 9					
City	D-48165 Münster	State	Germany		Zip		

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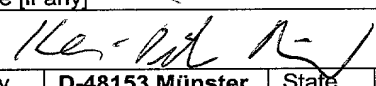
Name OF SECOND INVENTOR:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name (first and middle [if any]) Wilfried				Family Name or Surname STÜBBE			
Inventor's Signature <i>Wilfried Stübbe</i>				Date 30.10.01			
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Mailing Address		Niendamm 6					
City	D-48268 Greven	State	Germany		Zip		

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Name of Additional Joint Inventor, If any: <input type="checkbox"/> A petition has been filed for this unsigned inventor			
Given Name (first and middle [if any]) Heinz-Peter		Family Name or Surname RINK	
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